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Flame-Resistant Calenderable Polyester Resin and Resin Composition, and Sheet Obtained Using These Materials

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(54) [Title of the Invention]

**Flame-resistant Calenderable Polyester Resin
and Resin Composition, and Sheet Obtained
Using These Materials**

(57) [Summary]

[Object] To provide a calendered sheet of exceptional quality that has improved roll release properties when a polyester resin composition is calendered, which has hitherto proven difficult to achieve, and that has good flame resistance despite not containing any halogens.

[Means of Achievement] A flame-resistant calenderable polyester resin, characterized in that the content of phosphorus atoms in its molecular chain is 0.3 wt% or more, and the content of

aromatic dicarboxylic acids in the acid component is 60 mol% or more; a polyester resin composition obtained by means of compounding 0.01 to 5 weight parts lubricant with the polyester resin per 100 weight parts of the resin; and a sheet obtained using this composition.

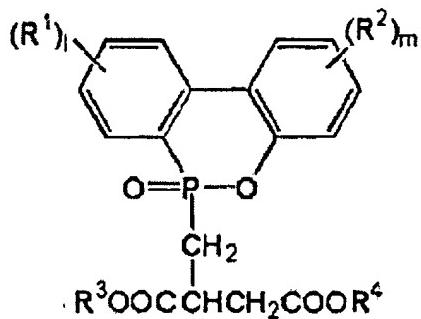
[Claims]

[Claim 1] A flame-resistant calenderable polyester resin, characterized in that the content of phosphorus atoms in the molecular chain thereof is 0.3 wt% or more, and the content of aromatic dicarboxylic acids in the acid component is 60 mol% or more.

[Claim 2] The flame-resistant calenderable polyester resin according to Claim 1, characterized in containing 30 mol% or more terephthalic acid with regard to the total carboxylic acid component, 30 mol% or more ethylene glycol component with regard to the total diol component, 5 to 70 mol% isophthalic acid with regard to the total dicarboxylic acid component, and/or 5 to 70 mol% of at least one diol component selected from the group comprising 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexane dimethanol with regard to the total diol component.

[Claim 3] The flame-resistant calenderable polyester resin according to Claim 1 or 2, obtained by means of copolymerizing a phosphorus-containing carboxylic acid indicated by general formula (I) or (II), or an ester compound thereof.

[Chemical Formula 1]

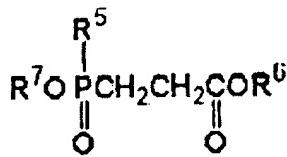


R^1, R^2 : Hydrogen atom or hydrocarbon group

R^3, R^4 : Hydrogen atom, hydrocarbon group, or hydroxy-substituted hydrocarbon group

l, m : Integer of from 0 to 4 inclusive

[Chemical Formula 2]



General Formula (II)

R⁵: Hydrogen atom or hydrocarbon group

R⁶, R⁷: Hydrogen atom, hydrocarbon group, or hydroxy-substituted hydrocarbon group

[Claim 4] A flame-resistant polyester resin composition for calendering, wherein 0.01 to 5 weight parts of a lubricant is compounded with the calenderable polyester resin according to Claims 1 to 3, per 100 weight parts of said polyester resin.

[Claim 5] The flame-resistant polyester resin composition for calendering according to Claim 4, wherein the lubricant is a polyolefinic wax and/or a metal salt of an organophosphate ester.

[Claim 6] A flame-resistant polyester resin composition for calendering, characterized in that 0.5 to 200 weight parts of a flame retardant is added to the polyester resin cited in Claims 1 to 3, or to the polyester resin composition cited in Claim 4 or 5, with regard to 100 weight parts of the polyester.

[Claim 7] Sheet obtained by means of calendering the polyester resin cited in Claims 1 to 3, or the resin composition cited in Claims 4 to 6.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a readily calenderable polyester resin and resin composition that have good roll release properties when polyester is calendered; that offer particularly exceptional non-halogen flame resistance in calendered sheet; and that are useful in various forms of sheet/film, and particularly in industrially machined sheet/film.

[0002]

[Prior Art] Vinyl chloride sheeting (film) is widely used in conventional practice in a variety of applications because of its low cost and excellent transparency. Extrusion molding and calender molding are known as methods for working this sheeting, but friction with the die lips in extrusion molding affects the workability (moldability) of the resin more than in calender

molding, which lowers the precision of the sheet (film) thickness, width, flow direction, and the like, and this method is ill-suited for large-scale production. The latter method is therefore more widely employed when productivity and quality are emphasized. However, due to drawbacks whereby dioxins are released during incineration of vinyl chloride, and restrictions on the use of plasticizers due to the presence of endocrine-disrupting chemicals, a changeover from vinyl chloride sheeting (film) to other materials has been underway in recent years. Among substitute materials, polyester is favored for its physical aspects, cost, and other attributes. However, using polyester as a substitute has the following significant drawback.

[0003] Polyester is poorly suited to calender molding, which is widely used as a method for molding vinyl chloride sheet. Extrusion molding has mainly been used conventionally as a method for manufacturing sheet and film from polyester resin for its ease of fabrication. However, molding is difficult when calendering is attempted using polyester resin, because of its relatively strong adhesion to the rolls when thermoplasticized, and its tendency to adhere to the rolls during fabrication. The addition of various lubricants has therefore been attempted in order to prevent adhesion to the rolls. Lubricants that have thus been investigated include, for example, polyethylene wax, paraffin wax, and other hydrocarbon lubricants; higher fatty acid lubricants, higher alcohol lubricants; metallic soaps made from higher fatty acids; fatty acid amide lubricants; ester lubricants; and various other lubricants. For example, amorphous polyethylene terephthalate copolymerized with cyclohexanedimethanol has been made into sheets by means of calendering with the aid of various lubricants, as described in JP (Kokai) Nos. 11-343353, 2000-136294, 2000-186191, 2000-302951, 2001-64496, 2001-4019, and US Patent No. 6068910.

[0004] Although it is possible to fabricate sheet by means of calendering amorphous polyethylene terephthalate copolymerized with cyclohexanedimethanol, such as described in the foregoing, major drawbacks are encountered when vinyl chloride resin is replaced with this polyester. Specifically, vinyl chloride resin has a high degree of flame resistance due to the effect of the chlorine atoms present in its molecules, but the molecular design of the aforementioned polyester was not intended to provide flame resistance. Accordingly, such polyesters have tended not to be introduced in applications such as casings for electrical appliances, decorative sheet for doors or wallpaper used in building materials, or similar occasions where flame resistance is demanded.

[0005]

[Problems Intended to Be Resolved by the Invention] With the foregoing issues in view, it is an object of the present invention to provide a flame-resistant calenderable polyester resin and resin composition that are endowed with improved roll release properties so as to ensure the desirable calenderability, and that offer exceptional flame resistance in calendered sheet despite not containing any halogens, and sheet in which such materials are employed.

[0006]

[Means Used to Solve the Above-Mentioned Problems] The present inventors conducted diligent investigations in an attempt to achieve the aforementioned object, and perfected the present invention based on the discovery that compounding a polyester resin that contained phosphorus atoms in its molecules, a lubricant, and (if required) a flame retardant would not only improve the roll release properties during calendering, but would also enable exceptional non-halogen flame resistance to be achieved. Specifically, the present invention has the characteristics described hereunder.

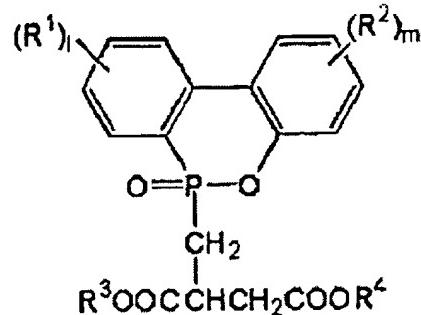
(1) A flame-resistant calenderable polyester resin, characterized in that the content of phosphorus atoms in the molecular chain thereof is 0.3 wt% or more, and the content of aromatic dicarboxylic acids in the acid component is 60 mol% or more.

(2) The flame-resistant calenderable polyester resin according to (1) above, characterized in containing 30 mol% or more terephthalic acid with regard to the total carboxylic acid component, 30 mol% or more ethylene glycol component with regard to the total diol component, 5 to 70 mol% isophthalic acid with regard to the total dicarboxylic acid component, and/or 5 to 70 mol% of at least one diol component selected from the group comprising 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexane dimethanol, with regard to the total diol component.

(3) The flame-resistant calenderable polyester resin according to (1) or (2) above, obtained by means of copolymerizing a phosphorus-containing carboxylic acid indicated by general formula (I) or (II), or an ester compound thereof.

[0007]

[Chemical Formula 3]



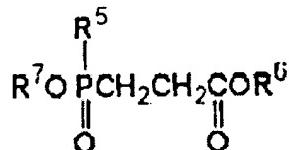
General Formula (I)

R¹, R²: Hydrogen atom or hydrocarbon group

R³, R⁴: Hydrogen atom, hydrocarbon group, or hydroxy-substituted hydrocarbon group

l, m: Integer of from 0 to 4 inclusive

[Chemical Formula 4]



General Formula (II)

R⁵: Hydrogen atom or hydrocarbon group

R⁶, R⁷: Hydrogen atom, hydrocarbon group, or hydroxy-substituted hydrocarbon group

[0008] (4) A flame-resistant polyester resin composition for calendering, wherein 0.01 to 5 weight parts of a lubricant is compounded with the polyester resin according to (1) to (3) above, per 100 weight parts of the polyester resin.

[0009] (5) The flame-resistant polyester resin composition for calendering according to (4) above, wherein the lubricant is a polyolefinic wax and/or a metal salt of an organophosphate ester.

[0010] (6) A flame-resistant polyester resin composition for calendering, characterized in that 0.5 to 80 weight parts* of a flame retardant is added to the polyester resin cited in (1) to (3) above, or to the polyester resin composition cited in (4) or (5) above, with regard to 100 weight parts of the polyester.

[0011] (7) Sheet obtained by means of calendering the polyester resin cited in (1) to (3), or the resin composition cited in (4) to (6).

* [Translator's note: the range in Claim 6, which corresponds to the present paragraph, is 0.5 to 200 weight parts.]

[0012]

[Embodiments of the Invention] It is essential for the calenderable polyester resin of the present invention to have 0.3 wt% or more phosphorus atoms contained in its molecular chain, and 60 mol% or more aromatic dicarboxylic acids in the acid component. If the phosphorus atom content is less than 0.3 wt%, it will not be possible to obtain adequate flame resistance. There are no particular limitations as to the upper limit, but from the perspectives of economic feasibility and polymerization, 8 wt% or less is preferable, and 5 wt% or less is more preferable. The amount of aromatic dicarboxylic acids contained in the acid component is 60 mol% or more, preferably 65 mol% or more, and ideally 70 mol% or more, as otherwise the mechanical properties of the calendered sheet will be diminished, hydrolyzability will suffer, and the molecular weight will decrease over time, which will lead to a deterioration in the physical properties of the sheet. Moreover, a further improvement in the flame resistance effect can be expected by increasing the concentration of aromatic rings. This phenomenon occurs because polyester resins are aromatic condensed resins, and oxygen-containing condensed resins in particular, and are therefore able to form a carbide coating, exhibiting self-extinguishing properties. Phosphorus-containing compounds are also copolymerized therewith, and these compounds, when burned, yield phosphoric acid and polyphosphoric acid in a solid phase and act as dehydrating agents, facilitating the formation of the carbide coating.

[0013] The polyester resin composition for calendering used in the present invention preferably contains 30 mol% or more terephthalic acid with regard to the total carboxylic acid component. An amount of 35 mol% or more is even more preferred, while an amount of 40 mol% or more is optimal. The mechanical properties of the sheet will deteriorate if less than 30 mol% terephthalic acid is contained in the resin composition, which is not preferred.

[0014] The polyester resin composition for calendering used in the present invention preferably contains 30 mol% or more of an ethylene glycol component with regard to the total diol component. An amount of 35 mol% or more is even more preferred, while an amount of 40 mol% or more is optimal. The mechanical properties of the sheet will deteriorate if less than 30 mol% ethylene glycol is contained in the resin composition, which is not preferred.

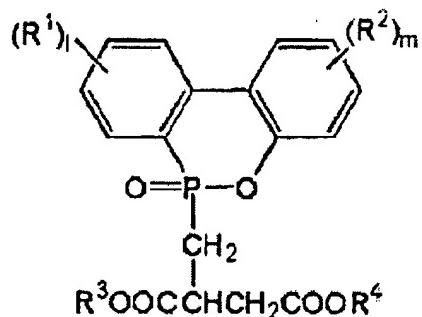
[0015] The polyester resin composition for calendering used in the present invention preferably contains 5 to 70 mol% isophthalic acid with regard to the total dicarboxylic acid component, and/or 5 to 70 mol% of at least one diol component selected from the group comprising

1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexane dimethanol, with regard to the total diol component. An upper limit of 65 mol% or more is even more preferred, while an amount of 60 mol% or more is optimal. A lower limit of 9 mol% or more is even more preferred, while an amount of 12 mol% or more is optimal. Suitability for calendering may be improved by means of appropriately introducing these copolymerizing components into the molecular chain, and appropriately adjusting the glass transition temperature, melting point, and softening point of the polyester resin. Among the above compounds, isophthalic acid, neopentyl glycol, diethylene glycol, and cyclohexane dimethanol are preferred from an economic standpoint, and copolymerizing 5 to 70 mol% neopentyl glycol is ideal when taking into consideration the affinity of the lubricant added to impart calenderability.

[0016] It is essential for phosphorus atoms to be introduced into the molecular chain of the calenderable polyester resin used in the present invention. The phosphorus-containing carboxylic acids indicated by general formula (I) or (II), or ester compounds thereof, are preferably copolymerized as monomers due to their wide availability.

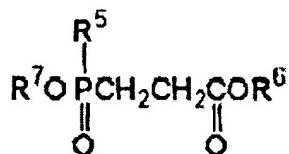
[0017]

[Chemical Formula 5]



[0018]

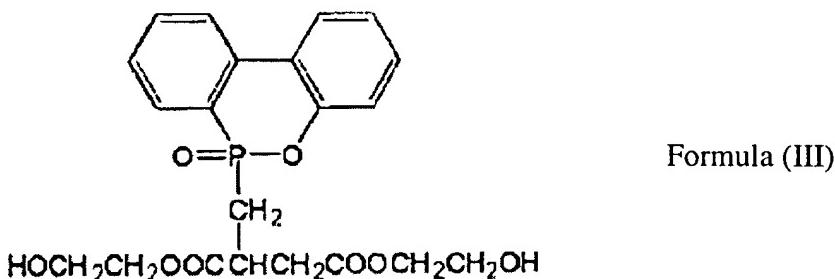
[Chemical Formula 6]



[0019] Specific examples of R¹ and R² include hydrogen atoms and hydrocarbon groups such as methyl, ethyl, propyl, and phenyl groups. R¹ and R² may either be the same or different. R³ and R⁴ may be hydrogen atoms and hydrocarbon groups or hydroxy-substituted hydrocarbon groups such as methyl, ethyl, propyl, butyl, phenyl, benzyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, and 2-hydroxyethoxyethyl groups. Specific examples of R⁵ include hydrogen atoms and hydrocarbon groups such as methyl, ethyl, propyl, and phenyl groups. R⁶ and R⁷ may be hydrogen atoms and hydrocarbon groups or hydroxy-substituted hydrocarbon groups such as methyl, ethyl, propyl, butyl, phenyl, benzyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, and 2-hydroxyethoxyethyl groups. Among the above groups, compounds indicated by Formula III are preferred for economic considerations.

[0020]

[Chemical Formula 7]



[0021] The calenderable polyester resin of the present invention may be copolymerized with a polyhydric carboxylic acid or polyhydric alcohol different from the terephthalic acid, isophthalic acid, ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexane dimethanol described in the foregoing. Examples of polyhydric carboxylic acids include orthophthalic acid, 1,5-naphthalene-dicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 2,2'-diphenyldicarboxylic acid, 4,4'-diphenyletherdicarboxylic acid, and other aromatic dibasic acids; and adipic acid, azelaic acid, sebacic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 4-methyl-1,2-cyclohexanedicarboxylic acid, dimer acids, trimellitic acid, and other aliphatic or alicyclic compounds. Examples of polyhydric alcohols include 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, dipropylene glycol, 2,2,4-trimethyl-1,5-pentanediol,

neopentyl hydroxypivalic ester, ethylene oxide adducts or propylene oxide adducts of bisphenol A, ethylene oxide adducts or propylene oxide adducts of hydrogenated bisphenol A, 1,9-nonanediol, 2-methyloctanediol, 1,10-decanediol, 2-butyl-2-ethyl-1,3-propanediol, tricyclo-decane dimethanol, polyethylene glycol, polypropylene glycol, and polytetramethylene glycol.

[0022] The number-average molecular weight of the calenderable polyester resin used in the present invention is preferably 15000 to 40000, more preferably 18000 to 35000, and ideally 20000 to 35000. If the number-average molecular weight is less than 15000, the strength and elongation of the sheet will be inadequate, due to inadequate resin cohesion, which makes it brittle and unusable. On the other hand, because the melt viscosity rises if the number-average molecular weight is 40,000 or above, the optimal temperature for calendering also rises, which results in poor roll release properties in the sheet.

[0023] The acid value of the calenderable polyester resin used in the present invention is preferably 60 eq/ 10^6 g or less, more preferably 50 eq/ 10^6 g or less, and ideally 40 eq/ 10^6 g or less. If the acid value exceeds 60 eq/ 10^6 g, hydrolysis will accelerate when the resin is heated during calendering, and the mechanical strength of the finished sheet will deteriorate. Moreover, the roll release properties will deteriorate as resin decomposition proceeds.

[0024] The melt viscosity of the calenderable polyester resin used in the present invention is preferably 3000 to 60000 dPa • sec, more preferably 4000 to 50000 dPa • sec, and ideally 5000 to 40000 dPa • sec at a shear rate of 100 sec⁻¹ and a temperature of 220°C. If the melt viscosity is less than 3000 dPa • sec, the adhesiveness of the resin will increase, and the roll release properties will diminish. On the other hand, a melt viscosity of greater than 60000 dPa • sec will be excessively high, and will prevent a practical degree of productivity from being attained.

[0025] A lubricant must be compounded with the polyester resin of the present invention when the resin is calendered to fabricate a sheet in order to realize improved roll release properties when the molten sheet is taken off from the rolls.

[0026] The amount of the lubricant used in the present invention to be compounded is 0.01 to 5 weight parts. The lower limit is preferably 0.05 weight parts, more preferably 0.1 weight parts, and ideally 0.2 weight parts, while the upper limit is preferably 4.5 weight parts, more preferably 4 weight parts, and ideally 3.5 weight parts. If the amount of lubricant is less than 0.01 weight parts, the effect of improving the roll release properties will be difficult to attain, while if the

amount exceeds 5 weight parts, diminished transparency, coloration, and printability of the worked sheet will tend to occur.

[0027] Examples of the lubricant used in the present invention include polyolefinic waxes, metal salts of organophosphate esters, organophosphate esters, ester compounds of higher aliphatic alcohols and adipic acid or azelaic acid, ethylene bisstearamide, methylene bisstearamide, glycerine higher fatty acid ester compounds, pentaerythritol higher fatty acid ester compounds, higher aliphatic alcohols, higher fatty acids, petroleum- or coal-derived paraffins, waxes, natural or synthetic polymer ester waxes, and metallic soaps based on higher fatty acids. The aforementioned lubricants may be used individually or in combinations of two or more. The use of a polyolefinic wax and/or a metal salt of an organophosphate ester is particularly preferred in order to readily establish a balance between the release properties of the sheet when taken off the rolls, and the transparency of the finished sheet.

[0028] Examples of polyolefinic waxes used as a lubricant in the present invention include polyethylene waxes, polypropylene waxes, and derivatives thereof. Examples of such derivatives include copolymers with other monomers such as acrylic acid, vinyl acetate, styrene, and maleic acid, and partially oxidized decomposition products.

[0029] Examples of metal salts of organophosphate esters used as a lubricant in the present invention include metal salts of organophosphate esters expressed by general formula (IV) below and/or metal salts of organophosphate esters expressed by general formula (V) below.

[0030] Formula (IV):

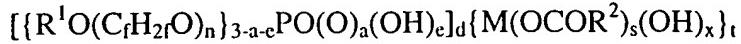


(wherein R is a hydrocarbon group having 4 to 30 carbons; M is an alkali metal, alkaline-earth metal, zinc, or aluminum; a is 1 or 2; e is 0 or 1 (but 0 or 1 when a is 1, and 0 when a is 2); b is 0 to 2; c is 1 or 2; d is 1 to 3; f is 2 or 3; n is 0 to 60; and a, b, c, and d have the following relationship with the valence (hereunder indicated as m) of the metal (M): when m = 1, then b = 0, d = 1, and a = c; when m is 2, then b = 0, c = 1, and a × d = 2, or b = 1, d = 1, and a = c; when m = 3, then b = 0, d = 3, a = c, b = 1, c = 1, and a × d = 2, or b = 2, d = 1, and a = c; and when m ≥ 2, then mutually different phosphate ion groups may also be bonded to the metal (M), in which case d = 2 or 3 is the total number of phosphate ion groups that are mutually different).

* [Translator's note: the "o" in the subscripted "3-a-o" may be a typographical error, since no explanation is provided for that symbol in the description following the formula. It is likely to be "e."]

Further, when d is 2 or 3, the respective structures in brackets may be the same or different from each other.)

[0031] Formula (V):



(wherein R¹ is a hydrocarbon group having 4 to 30 carbons; R² is an alkyl group having 1 to 25 carbons; M is an alkali metal, alkaline-earth metal, zinc, or aluminum; a is 1 or 2; e is 0 or 1 (but is 0 or 1 when a is 1, and is 0 when a is 2); d = 1 or 2; s is 1 or 2; x is 0 or 1; t is 1 or 2; f is 2 or 3; and n is 0 to 60. s + x = 1 or 2, and a, d, s, and t have the following relationship with the valence (hereunder indicated as m) of the metal (M): when m = 2, then s = 1, d = 1, and a = t; when m = 3, then s = 1, t = 1, and a × d = 2, or s = 2, d = 1, and a = t; and when m = 3, then mutually different phosphate ion groups may be bonded with the metal (M), in which case d = 2 signifies the total number of phosphate ion groups. Furthermore, when d is 2, the respective structures in brackets may be the same or different from each other.)

[0032] Alkyl groups, phenyl groups, arylalkyl groups, alkenyl groups, or alkyl phenyl groups are preferred as the hydrocarbon groups having 4 to 30 carbons indicated by R in general formula (IV) and as the hydrocarbon groups having 4 to 30 carbons indicated by R¹ in general formula (V). Preferred examples of the alkali metals that are represented by M in general formula (IV) and general formula (V) include lithium, sodium, and potassium, and preferred examples of the alkaline-earth metals include magnesium, calcium, and barium.

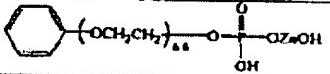
[0033] The metal salts of the organophosphate esters expressed by general formula (IV) and the metal salts of the organophosphate esters represented by general formula (V) may be manufactured by means of common methods, and there are no particular limitations as regards such methods of manufacture.

[0034] Preferred examples of the metal salts of the organophosphate esters represented by general formula (IV) include compounds (1) to (13) in Table 1 below and compounds (14) to (16) in Table 2 below. Preferred examples of the metal salts of the organophosphate esters represented by general formula (V) include compounds (15) to (26) in Table 2 below. These compounds may be used individually or in combinations of two or more. Also, as shown by decimal fractions included in the number of repetitions of oxyethylene or oxytrimethylene units in the polyether alcohol component, these compounds (compounds (1) through (26)) are pure compounds or mixtures of a plurality of metal salts of phosphate esters having different numbers

of repeating oxyethylene units or oxytrimethylene units in the polyether alcohol component (the number of repetitions (n) in $(C_2H_2O)_n$ in the formula).

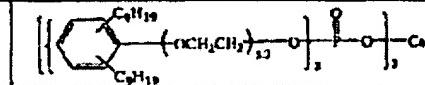
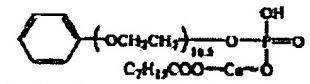
[0035]

[Table 1]

Cpd. no.	Structural formula	Cpd. no.	Structural formula
(1)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{ONa}$	(9)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{ZnOH} \right]_n$
(12)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{2,3}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{Na}$	(10)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{OH} \right]_n$ $C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{4,5}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{Na}$
(13)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{Ca}}{\text{P}}}=\text{O}-\text{O}-\text{Ca}$		
(14)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{3,4}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{Mg(OH)}$		
(15)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{4,5}-O-\overset{\text{O}}{\underset{\text{O}-\text{NaOH}}{\text{P}}}=\text{O}-\text{O}-\text{Na}$	(11)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{Me}}{\text{P}}}=\text{O}-\text{O}-\text{Me} \right]_n$ $C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{4,5}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{OH}$
(16)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{K}}{\text{P}}}=\text{O}-\text{O}-\text{K} \right]_n$		
(17)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{Zn}}{\text{P}}}=\text{O}-\text{O}-\text{Zn} \right]_n$	(12)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{O}-\text{OH}$
(18)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{6,7}-O-\overset{\text{O}}{\underset{\text{O}-\text{Zn}}{\text{P}}}=\text{O}-\text{O}-\text{Zn}$	(13)	

[0036]

[Table 2]

Cpd no.	Structural formula	Cpd no.	Structural formula
(14)	$C_{12}H_{22}\left\{-OCH_2CH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{OH}}{\text{P}}}=\text{O}-\text{ONa}$	(21)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{D}}{\text{P}}}=\text{O}-\text{O}-\text{D}$ $C_{12}H_{22}\text{COO}-\text{Al}$
(15)		(22)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{CH}_2\text{COO}-\text{Al(OH)}}{\text{P}}}=\text{O}-\text{O}-\text{CH}_2\text{COO}-\text{Al(OH)} \right]_n$
(16)	$C_{12}H_{22}\text{O}-\overset{\text{O}}{\underset{\text{O}-\text{Zn}}{\text{P}}}=\text{O}-\text{O}-\text{Zn}$	(23)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Zn}}{\text{P}}}=\text{O}-\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Zn} \right]_n$
(17)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Br}}{\text{P}}}=\text{O}-\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Br}$	(24)	
(18)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Mg}}{\text{P}}}=\text{O}-\text{O}-\text{Mg}$	(25)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Br}}{\text{P}}}=\text{O}-\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Br} \right]_n$
(19)	$C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Ca}}{\text{P}}}=\text{O}-\text{O}-\text{Ca}$	(26)	$\left(C_{12}H_{22}\text{O} \right)_2-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Zn}}{\text{P}}}=\text{O}-\text{O}-\text{Zn} \right)_n$
(20)	$\left[C_{12}H_{22}\left\{-OCH_2CH_2\right\}_{1,2}-O-\overset{\text{O}}{\underset{\text{O}-\text{C}_2\text{H}_5\text{COO}-\text{Zn}}{\text{P}}}=\text{O}-\text{O}-\text{Zn} \right]_n$		

[0037] The flame-retardant effect of the phosphorus-containing polyester resin may be heightened by means of using a phosphorus-, nitrogen-, hydrated-metal, inorganic, or silicon-based flame retardant in combination with the polyester resin and resin composition used in the present invention. Examples include phosphorus-based flame retardants such as triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, triethyl phosphate, cresyl diphenyl phosphate, xylene diphenyl phosphate, cresyl *bis*(2,6-xylene) phosphate, 2-ethylhexyl phosphate, dimethylmethyl phosphate, resorcinol bis(diphenyl) phosphate, bisphenol A bis(diphenyl) phosphate, bisphenol A *bis*(dicresyl) phosphate, diethyl-N,N-bis(2-hydroxyethyl)aminomethyl phosphate, phosphoric amide, organophosphine oxide, and red phosphorus; nitrogen-based flame retardants such as ammonium polyphosphate, phosphazene, cyclo-phosphazene, triazine, melamine cyanurate, succinoguanamine, ethylene dimelamine, triguanamine, triazinyl cyanurate salt, melem, melam, *tris*(β -cyanoethyl)isocyanurate, acetoguanamine, guanyl sulfate melamine, melem sulfate, and melam sulfate; metal salt-based flame retardants such as potassium diphenylsulfone-3-sulfonate, metal salts of aromatic sulfonimides, and alkali metal salts of polystyrenesulfonic acid; hydrated metal flame retardants such as aluminum hydroxide, magnesium hydroxide, dolomite, hydrotalcite, barium hydroxide, basic magnesium carbonate, zirconium hydroxide, and tin oxide; inorganic flame retardants such as silica, aluminum oxide, iron oxide, titanium oxide, manganese oxide, magnesium oxide, zirconium oxide, zinc oxide, molybdenum oxide, cobalt oxide, bismuth oxide, chromium oxide, tin oxide, antimony oxide, nickel oxide, copper oxide, tungsten oxide, zinc borate, zinc metaborate, barium metaborate, zinc carbonate, magnesium carbonate, calcium carbonate, barium carbonate, and zinc stannate; and silicon-based flame retardants such as silicone powder. A profound flame-retardant effect is derived from the combination of the flame-retarding mechanism of the flame retardants and the high flame resistance of the phosphorus compound-containing resin itself. The upper limit of the amount to be compounded per 100 weight parts polyester resin is preferably 200 weight parts, more preferably 180 weight parts, and ideally 150 weight parts in consideration of the mechanical properties of the finished sheet. The lower limit is 0.5 weight parts.

[0038] Other components may also be appropriately added to the polyester resin composition of the present invention according to the application. Examples of such components include fillers,

UV absorbers, photostabilizers, pigments, antistatic agents, antibacterial agents, epoxy compounds, and crosslinking agents.

[0039]

[Working Examples] The present invention is described in detail below with reference to working examples; however, the present invention shall not be construed to be limited to these examples. The measurement values described in the synthesis examples were obtained according to the following methods.

[0040] Resin composition: The resin was dissolved in heavy chloroform and the composition was determined according to H-NMR.

[0040] Glass transition point: A differential scanning calorimeter was used, and 10 mg of a measurement sample was introduced into an aluminum pan, which was then covered and sealed. Measurements were made at a temperature elevation rate of 20°C/min.

Number-average molecular weight: Determined as a value converted for polystyrene by means of gel permeation chromatography, using hexafluoroisopropanol as a solvent.

Acid value: Determined by means of dissolving one gram of resin in 30 mL of chloroform and performing titration with a 0.1 N potassium hydroxide ethanol solution. Phenol phthalein was used as the indicator.

[0041] Phosphorus atom content (determined according to wet decomposition/molybdenum blue colorimetry)

A sample was measured into a three-neck flask in conformity with the phosphorus concentration of the sample. 3 mL sulfuric acid, 0.5 mL perchloric acid, and 3.5 mL nitric acid were added thereto, and the resulting mixture was subjected to mild heat-induced decomposition over half a day using an electric heater. The solution was heated further once becoming transparent, until white sulfuric acid fumes were produced. The decomposed solution was left to cool to room temperature, after which 50 mL of the solution was transferred into a measuring flask. 5 mL of a 2% ammonium molybdate solution and 2 mL of a 0.2% hydrazine sulfate solution were added thereto, the flask was topped up with purified water, and the contents were thoroughly mixed. The flask was then placed in a bath of boiling water for ten minutes, heated until color had developed, then cooled to room temperature with water, and ultrasonically degassed. A sample of the solution was transferred to a 10 mm absorption cell, and its light absorbance was measured with a spectrophotometer (wavelength: 830 nm) using a blank

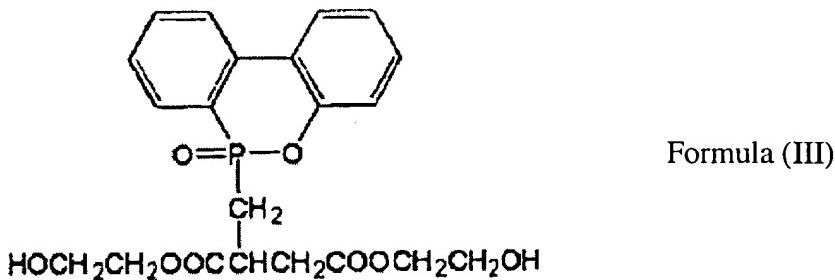
test solution as a control. The phosphorus content was determined according to a calibration curve that had been prepared beforehand to calculate the concentration of phosphorus in the sample.

[0042] (Polyester Synthesis Example 1)

4250 weight parts terephthalic acid, 1930 weight parts dimethyl isophthalate, 820 weight parts ethylene glycol, 4290 weight parts neopentyl glycol, and 2.7 weight parts tetrabutyl titanate were added into a reaction vessel fitted with a stirrer, temperature gauge, and distillation cooler, and transesterified for two hours at 170 to 220°C. Once transesterification was complete, 6920 weight parts of a solution of the ethylene glycol indicated by Formula III (GHM-1; manufactured by Sanko Co., Ltd.; solid fraction concentration: 50%) was added into the reaction system. The temperature was again elevated to 220°C while the system was stirred for ten minutes. Once the temperature had reached 220°C, the temperature was elevated further to 270°C, while the pressure in the system was gradually reduced, until a level of 500 Pa had been attained after 60 min. Polycondensation was subsequently performed for 55 min at 130 Pa or less to obtain the copolyester for Synthesis Example 1.

[0043]

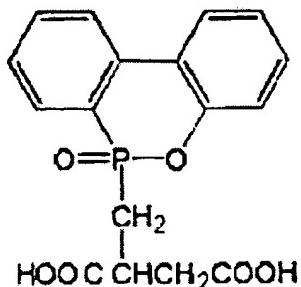
[Chemical Formula 8]



[0044] Polyester Synthesis Example 1 was analyzed using NMR, which revealed a composition in which the dicarboxylic acid component was 55 mol% terephthalic acid, 25 mol% isophthalic acid, and 20 mol% of the component indicated by Formula VI (recorded in the table as a dicarboxylic acid for convenience), and in which the diol component was 51 mol% ethylene glycol and 49 mol% neopentyl glycol. The glass transition point was 68°C, the number-average molecular weight 28000, the acid value 30 eq/10⁶ g, and the phosphorus content 2.9 wt%.

[0045]

[Chemical Formula 9]



[0046] Polyester Synthesis Examples 2 through 6 and Comparative Synthesis Examples 1 through 3 were manufactured in the same manner as Polyester Synthesis Example 1. The compositions and measurement results are all shown in Table 3 (the numerals refer to mol% in the resin).

[0047]

[Table 3]

		SE1	SE2	SE3	SE4	SE5	SE6	CSE1	CSE2	CSE3
Acid component	Terephthalic acid	55	74	68	55	92	79	90	100	99
	Isophthalic acid	25		21	25			10		
	Adipic acid						5			
	Formula VI	20	26	11	20	8	16			1
Glycol component	Ethylene glycol	51	70	100	55	66	82	75	70	70
	1,2-Propanediol				12					
	1,3-Propanediol					14				
	1,4-Butanediol						18			
	2-Methyl-1,3-propanediol					20				
	Neopentyl glycol	49						25		
	Diethylene glycol				23					
	Cyclohexane dimethanol		30						30	30
Number-average molecular weight		28000	30000	26000	23000	20000	35000	28000	27000	29000
Glass transition temperature (°C)		68	72	70	57	59	55	75	78	78
Acid value (eq/t)		30	28	14	26	32	34	15	18	22
Phosphorus content (wt%)		2.9	3.3	1.8	2.7	1.0	2.5	0	0	0.2

[“SE” = synthesis example; “CSE” = comparative synthesis example]

[0048] The polyesters shown in Table 3 were mixed in a beaker with each of the components shown in Tables 4 and 5, and the resulting mixtures were kneaded on two 6-inch chilled rolls that had been set to 180°C. The mixing was performed while any resin that had adhered to the chilled rolls was periodically removed with a spatula. Kneading was performed for a further five minutes, after which the gap between the rolls was set to 0.3 mm (i.e., the sheet thickness was set to 0.3 mm), and the release properties of the molten sheet were evaluated as it was taken off from the rolls. The standards for the evaluations were as provided below. The results are shown in Tables 4 and 5.

[0049] Release properties of sheet: "A" (released satisfactorily from rolls) and "B" (sheet adhered tightly to rolls; problems encountered with release; normal sheet unobtainable).

Flame resistance: Evaluated using the limiting oxygen index (LOI) according to the oxygen index method of JIS K7201. This represents the minimum oxygen concentration required for the sample to burn. A higher oxygen index reflects a higher flame resistance.

The lubricants and flame retardants cited in Tables 4 and 5 refer to the following compounds.

- a: Zinc salt of tridecyl poly(oxyethylene)phosphate
- b: Styrene-modified polyethylene wax
- c: Aluminum hydroxide
- d: Ammonium polyphosphate

All figures for the amounts of polyesters, lubricants, and flame retardants in the tables are given in parts by weight.

[0050]

[Table 4]

		Working Examples								
		1	2	3	4	5	6	7	8	9
Copolyester	Synthesis Example 1	100						100	100	100
	Synthesis Example 2		100							
	Synthesis Example 3			100						
	Synthesis Example 4				100					
	Synthesis Example 5					100				
	Synthesis Example 6						100			
Evaluation	Flame Lubri-cant	a	1	0.8	2.1		1.1	0.5	1	1
		b	0.5	0.4		1.3	1.1	0.5	0.5	0.5
		c					35		14	
		d						42	28	67
	Sheet release properties	A	A	A	A	A	A	A	A	A
	Flame resistance (LOI)	34	36	32	33	36	38	42	44	48

[0051]

[Table 5]

		Comparative Examples			
		1	2	3	4
Copoly-ester	Synthesis Example 1	100			
	Comparative Synthesis Example 1		100		
	Comparative Synthesis Example 2			100	
	Comparative Synthesis Example 3				100
Evaluation	Flame Lubri-cant	a		0.8	2.1
		b		0.4	
		c			5.0
		d			
	Sheet release properties	B	A	A	A
	Flame resistance (LOI)	33	22	24	25

[0052]

[Effect of the Invention] As has been described in the foregoing, the polyester resin of the present invention and composition thereof contain a combination of a polyester with phosphorus atoms in its molecular chain, a lubricant, and (if required) a flame retardant, and this composition is therefore able to improve the release properties of sheet taken off from rolls when polyester resin compositions are calendered, which has hitherto proven problematic, and also to yield

calendered sheet having exceptional quality and good flame resistance despite not containing any halogens.

F Terms (Reference):

4F071 AA14 AA44 AA71 AA80 AA81

AA86 AB18 AB25 AC15 AE11

AF30 AF47 AF53 AH19 BA01

BB04 BC01

4F204 AA24E AB05 AB07 AB19

FA06 FB02 FE21 FF01 FN11

FN15 FN20

4J002 BB042 BB122 BB252 CF031

CF041 DA057 DE037 DE067

DE077 DE097 DE107 DE127

DE147 DE187 DE217 DE237

DE267 DE287 DH047 DH057

DJ017 DK007 EA016 EC066

EF056 EG016 EH046 EH056

EH096 EP026 EU187 EU197

EV257 EW026 EW046 EW047

EW126 EW147 EW157 FD137

FD172 FD176

4J029 AA03 AB01 AD01 AD02 AD05

AD07 AD10 AE01 BA03 BA04

BA05 BA09 BA10 BD07A

BF09 BF10 BF21 BF24 BF26

BH03 CA02 CA06 CB04A

CB05A CB06A CB10A CC01

CC05A CC06A CD03 CD04

FB03 FB18 FC36 GA11 HA01

HB01 HB03A HD04 JB131

JF251 KD02 KD07 KE02

KE05